

We Claim:

- Sub 1
1. A process for the production of lower aliphatic esters said process comprising reacting a lower olefin with a saturated lower aliphatic mono-carboxylic acid in the vapour phase in the presence of a heteropolyacid catalyst characterised in that an amount of water in the range from 1-10 mole % based on the total of the olefin, aliphatic mono-carboxylic acid and water is added to the reaction mixture during the reaction.
  2. A process according to Claim 1 wherein the amount of water added is in the range from 1 to 7 mole % based on the total of the olefin, aliphatic mono-carboxylic acid and water.
  - 10 3. A process according to Claim 1 wherein the amount of water added is in the range from 1 to 5 mole % based on the total of the olefin, aliphatic mono-carboxylic acid and water.
  - Sub 2
  - ~~4. A process according to Claim 1 wherein the heteropolyacid catalyst is supported on a siliceous support which is in the form of extrudates or pellets.~~
  - 15 5. A process according to Claim 4 wherein the siliceous support is derived from an amorphous, non-porous synthetic silica.
  6. A process according to Claim 4 wherein the siliceous support is derived from fumed silica produced by flame hydrolysis of  $\text{SiCl}_4$ .
  - ~~7. A process according to Claim 4 wherein the siliceous supports is Support 350 made by pelletisation of AEROSIL® 200 (both ex Degussa).~~
  - 20 ~~7/8.~~ 8. A process according to Claim 4 wherein the silica support is in the form of pellets or beads or are globular in shape having an average particle diameter in the range from 2 to 10 mm, a pore volume in the range from 0.3-1.2 ml/g, a crush strength of at least 2 Kg force and a bulk density of at least 380 g/l.
  - 25 ~~9/9.~~ 9. A process according to Claim 4 wherein the siliceous support has at least 99%

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w/w purity.

9. A process according to Claim 4 wherein the siliceous support is a pelleted silica support which has an average bulk density of about 0.39 g/ml, an average pore volume of about 1.15 ml/g and an average particle size ranging from about 0.1-3.5 mm.

10. A process according to Claim 10 wherein the pelleted silica support is used as such or after crushing to an average particle size in the range from 0.5-2 mm to support the heteropolyacid catalyst.

11. A process according to Claim 1 wherein the heteropolyacids used to prepare the esterification catalyst is selected from the free acids and co-ordination-type salts thereof in which the anion is a complex, high molecular weight entity and comprises 2-18 oxygen-linked polyvalent metal peripheral atoms surrounding in a symmetrical manner a central atom or ion from Groups I-VIII in the Periodic Table of Elements.

12. A process according to Claim 12 wherein the peripheral atom is one or more of molybdenum, tungsten, vanadium, niobium and tantalum and the central atom or ion is selected from silicon; phosphorus; cupric ions; divalent beryllium, zinc, cobalt or nickel ions; trivalent boron, aluminium, gallium, iron, cerium, arsenic, antimony, phosphorus, bismuth, chromium or rhodium ions; tetravalent silicon, germanium, tin, titanium, zirconium, vanadium, sulphur, tellurium, manganese nickel, platinum, thorium, hafnium, cerium ions and other rare earth ions; pentavalent phosphorus, arsenic, vanadium, antimony ions; hexavalent tellurium ions; and heptavalent iodine ions.

13. A process according to Claim 1 wherein the heteropolyacids have a molecular weight eg in the range from 700-8500 and include dimeric complexes.

14. A process according to Claim 1 wherein the heteropolyacid comprises at least one of the following compounds:

12-tungstophosphoric acid	-	$H_3[PW_{12}O_{40}].xH_2O$
12-molybdophosphoric acid	-	$H_3[PMo_{12}O_{40}].xH_2O$
12-tungstosilicic acid	-	$H_4[SiW_{12}O_{40}].xH_2O$
12-molybdosilicic acid	-	$H_4[SiMo_{12}O_{40}].xH_2O$
Potassium tungstophosphate	-	$K_6[P_2W_{18}O_{62}].xH_2O$
Sodium molybdophosphate	-	$Na_3[PMo_{12}O_{40}].xH_2O$
Ammonium molybdodiphosphate	-	$(NH_4)_6[P_2Mo_{18}O_{62}].xH_2O$
Sodium tungstonickelate	-	$Na_4[NiW_6O_{24}H_6].xH_2O$
Ammonium molybdodicobaltate	-	$(NH_4)_4[Co_2Mo_{10}O_{36}].xH_2O$
Cesium hydrogen tungstosilicate	-	$Cs_3H[SiW_{12}O_{40}].xH_2O$
Potassium molybdodivanado phosphate	-	$K_5[PMoV_2O_{40}].xH_2O$

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~~16~~ A process according to Claim 4 wherein the amount of heteropolyacid deposited/impregnated on the support for use in the esterification reaction is in the range from 10 to 60% by weight based on the total weight of the heteropolyacid and the support.
- 5 ~~13~~  
~~17~~ A process according to Claim 1 wherein the olefin reactant used is ethylene, propylene or mixtures thereof.
- ~~14~~  
~~18~~ A process according to Claim 1 wherein the saturated, lower aliphatic mono-carboxylic acid reactant is a C1-C4 carboxylic acid.
- ~~15~~  
~~19~~ A process according to Claim 1 wherein the aliphatic mono-carboxylic acid reactant is acetic acid.
- 10 ~~16~~  
~~20~~ A process according to Claim 1 wherein the reaction mixture has a molar excess of the olefin reactant with respect to the aliphatic mono-carboxylic acid reactant.
- ~~17~~  
~~21~~ A process according to Claim 1 wherein the mole ratio of olefin to the lower carboxylic acid in the reaction mixture is in the range from 1:1 to 15 : 1.
- 15 ~~18~~  
~~22~~ A process according to Claim 1 wherein the mole ratio of olefin to the lower carboxylic acid in the reaction mixture is in the range from 10:1 to 14:1.
- ~~19~~  
~~23~~ A process according to Claim 1 wherein the reaction is carried out in the vapour phase above the dew point of the reactor contents comprising the reactant acid, any alcohol formed *in situ*, the product ester and water.
- 20 ~~20~~  
~~24~~ A process according to Claim 1 wherein the supported heteropolyacid catalyst is used as a fixed bed which is in the form of a packed column.
- ~~21~~  
~~25~~ A process according to Claim 1 wherein the heteropolyacid catalyst is further modified by the addition of phosphoric acid or other mineral acids thereto.
- 25 ~~22~~  
~~26~~ A process according to Claim 1 wherein the vapours of the reactant olefins and acids are passed over the catalyst at a GHSV in the range of 100 to 5000 per hour.
- ~~23~~  
~~27~~ A process according to Claim 1 wherein the esterification reaction is carried out at a temperature in the range from 150-200°C using a reaction pressure which is at least 400KPa.
- 30 28. A process according to Claim 1 wherein the reaction mixture is dosed with a di-ether amount of a di-ether co-fed is suitably in the range from 1 to 6 mole % based on the total reaction mixture comprising the olefin, the aliphatic carboxylic acid, water and di-ether.
- 35 29. A process according to Claim 28 wherein the di-ether corresponds to the

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by-product di-ether formed *in situ* during the reaction from the reactant olefin which is recovered and is recycled to the reaction mixture.

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A process according to Claim ~~28~~<sup>24</sup> wherein the di-ether is diethyl ether.

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ether. A process according to Claim ~~28~~<sup>24</sup> wherein the di-ether is an unsymmetrical

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